A Corrosion Resistant Coating For IVD Aluminum

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INTRODUCTION

Conversion coating is the chemical treatment of a metal surface to produce an adherent coating composed of protective chemicals which primarily inhibit corrosion and increase paint adhesion, while providing acceptable contact electrical resistance. Chromate conversion coatings (CCC) are produced by combining chromium compounds, identified as one of the U.S. Environmental Protection Agency's (EPA) top 17 worst industrial toxins, with other water-soluble inorganic materials. Non-Chromate conversion coatings (NCCC) are produced by using various non-chromium containing compounds to perform the same function as the current CCC.

In 1993, McDonnell Douglas Aerospace East (MDA-E), was contracted by the U.S. Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/MLQE) to identify a non-chromate alternative to the conventional chromate conversion coating for ion vapor deposition (IVD) aluminum. A Final Report was issued by MDA-E detailing the testing and recommendation of the NCCC for further testing and optimization.[1] AFRL/MLQE is now working with Warner-Robins Air Logistics Center (WR-ALC), ARCADIS Geraghty & Miller, and Battelle Memorial Institute to demonstrate and validate the NCCC chemistry for IVD Aluminum recommended by MDA-E. The MDA-E-recommended NCCC chemistry is commercially available from Sanchem. The project objective is to further develop, test, and evaluate the performance of the Sanchem SafeGard™ CC 3000 Sealing Step II, followed by Sealing Step III as compared to the current CCC. The environmental advantage of this novel technique is primarily pollution prevention with an elimination in Cr^{+6} hazardous waste generation and subsequent disposal, while maintaining the required quality of conversion coating as stated in the military specifications. This paper will provide results from the bench scale optimization testing, a discussion of the pilot testing, and current results from the Engineering and Manufacturing Development (EMD) testing.

BACKGROUND

MDA-E surveyed the industry/DoD and identified twelve candidate non-chromate conversion coating processes for potential use with IVD aluminum. Based on internal MDA-E data, six processes were identified and screened using Class 2 (0.5 mil minimum thickness) IVD aluminum coated AISI 4130 steel panels. The panels were exposed to neutral salt fog, primer adhesion, and contact electrical resistance tests. The process based on Sanchem's Sealing Step II, a potassium permanganate ($KMnO_4$) solution immersion at 140 F for one minute, performed well in these tests with no failure at 3,000-h salt fog exposure, minor failure of scribed, wet, paint adhesion, and acceptable contact electrical resistance. Supplementary tests were run with Class 2 coated panels using variations on Sealing Step II.

Based on the results of the screening tests, four non-chromate conversion coatings were selected for expanded corrosion resistance testing by MDA-E including two variations on Sealing Step II. Class 1 (1.0 mil

[1]Fournier, J.A. and J.J. Reilly, A Determination of the Effectiveness of Nonchromate Conversion Coatings for Use with IVD Aluminum Coatings, October 1995.

minimum thickness) IVD aluminum coated AISI 4130 steel panels were treated and subjected to neutral salt fog testing, sulfur dioxide (SO_2) salt fog testing, and extended outdoor exposure. Aluminum alloy panels, steel fasteners, and titanium fasteners were also coated with IVD aluminum and tested with the four candidate non-chromate conversions coatings. The parts were evaluated for corrosion resistance to neutral salt fog and SO_2 salt fog. These results led to selection of a Sealing Step II process and a process consisting of Sealing Step II followed by Sealing Step III (hot potassium silicate solution immersion) for optimization on a bench-scale pilot production line.

TEST PLAN DESIGN

A test plan was designed for an optimization task using a laboratory bench-scale system and for Engineering and Manufacturing Development (EMD) qualification using a pilot-scale system installed in the plating shop at WR-ALC. The optimization test plan consisted of five sets of experiments: baseline, screening, optimization, operability, and validation. The EMD qualification test included operating the pilot line at the initial recommended conditions and then at process conditions identified by the optimization experiments.

Both test panels and condemned components were included in the testing. Panels used for testing were AISI 4130 steel (4 x 6 x 0.050 inches) with a standard mill finish. Panels were visually inspected and any with significant defects were rejected; accepted panels were shipped to WR-ALC for application of a Class 1 aluminum coating (>0.001 inch thick) by the IVD process. A nominal thickness of 0.0011 inches was provided on the panels. WR-ALC personnel performed all steps of the IVD process, including degreasing, aluminum oxide grit blasting, IVD, and glass bead peening. Panels received a conversion coating within 24 hours after glass bead peening. Condemned components were provided and prepared by WR-ALC.

Test methods utilized included electrical impedance spectroscopy (EIS), neutral salt fog (ASTM B117), contact electrical resistance (MIL-C-81706), and paint adhesion (ASTM D339 and Method 8301 of Federal Test Method Standard No. 141). Panels processed during the optimization task were tested using EIS to quickly obtain performance results. Also, two sets of test panels were tested by neutral salt fog for comparison with MDA-E results. EMD qualification testing consisted of 1344 hours exposure to neutral salt fog, dry and wet adhesion tests using panels coated with one of three primers (epoxy primers MIL-P-23377 Type 1 Class 2, or MIL-P-85582 Type 1 Class N, or polyurethane primer TT-P-2760 Type 1 Class 2), and contact electrical resistance. The MIL-C-83488 requirement for corrosion resistance for Class 1 IVD aluminum with CCC is 672 hours exposure to salt fog (ASTM B117) without the appearance of base metal corrosion.

OPTIMIZATION TEST RESULTS

The increased corrosion resistance achieved by raising the temperature of the Sealing Step II bath observed by MDA-E was also observed during optimization testing. Improved corrosion protection was observed with reduced concentration of the Sealing Step III bath. The initial recommended process conditions were adjusted by increasing the operating temperature of the Sealing Step II bath from 145 F to 165 F and reducing the concentration of the Sealing Step III bath from 8.1 percent to 7.0 percent.

Operability experiments were performed to investigate questions regarding long-term process operation. First, a test was performed to investigate the effects of reducing the temperature of the Sealing Step III bath from the recommended 200 F. Panels were processed at 180 F and 200 F, cross-sectioned and examined using a scanning electron microscope. The panels processed at the lower temperature appeared to have poorer bonding to the substrate. This was consistent with Sanchem's claim that a lower temperature would result in a coarse-grained potassium aluminum silicate layer. Therefore, it was concluded that the Sealing Step III bath should be operated at the recommended conditions of 190 F to 212 F.

A second operability experiment determined that standard plating shop bath filtration procedures should be sufficient to maintain process quality. The experiment investigated whether potassium aluminum silicate solid byproduct in the Sealing Step III bath would adhere to the applied coating and, if removed during handling, reduce the effectiveness of the coating. Panels were processed through a bath with high levels of byproducts. Despite

attempts to force adherence by immersing panels as close to horizontal as possible, no particle embedding was observed. Therefore, solid byproducts are not believed to be a concern, but should be removed by filtration.

The final operability experiment determined that contamination of the Sealing Step II bath with solution from the Sealing Step III bath did not result in any visual difference in the applied coatings. Sanchem warns that such cross-contamination may reduce the effectiveness of the conversion coating. A Sealing Step II bath was contaminated with Sealing Step III bath solution to simulate a 1 ppm contamination level. Panels were processed in the contaminated solution and uncontaminated solution followed by the Sealing Step III solution. Visual inspection did not show any significant difference in surface color or drainage pattern. Based on Sanchem's warning, operating practice should be to avoid any contact of the Sealing Step III solution with the Sealing Step II bath by thorough rinsing of fixtures after processing.

An experiment was conducted to investigate the elapsed time between glass bead peening and conversion coating. There was no significant corrosion resistance difference between panels which were conversion coated with SafeGard™ at either 24 or 48 hours after glass bead peening. However, to ensure consistent product, the elapsed time between glass bead peening and conversion coating should continue to be controlled as is currently done with CCC.

Another experiment investigated the effect of preconditioning on corrosion resistance of the panels. Corrosion resistance was significantly lower between panels preconditioned using Sanchem 550 (1 percent phosphoric acid) and panels with no preconditioning prior to processing with the SafeGard™ process at initial recommended conditions. The reduced performance is believed to be related to the attack of the acid on the aluminum metal and oxide coating of the IVD aluminum causing porosity. Therefore, it was concluded that preconditioning is undesirable.

The variability in porosity of the IVD aluminum appeared to be a significant cause of variability in the corrosion resistance performance. Porosity variability was observed as a difference in coloration of panels processed through chromate conversion coating. Panels ranged in color from bright gold to gray. Interviews of shop personnel indicated that color correlated with the glass bead peening process, with a more thorough glass bead peening process yielding the gold color. It is believed that the manual peening process performed was variable and could be the cause of observed corrosion resistance variability.

PILOT OPERATION AND TESTING

A pilot line was designed and installed at WR-ALC plating shop, Building 142. The design was based on the results from the optimization testing and the configuration partially required by the Sanchem Sealing Steps II and III. A dormant plating line was reconfigured and additional equipment was installed to provide essential resources not available from the base plating shop.

Design

The pilot demonstration line consisted of four 200 gallon stainless steel tanks oriented to provide sequential immersion in each bath. Two of the tanks, 410 and 414, were lined with a polyethylene mesh and were used as rinse tanks. Tanks 409 and 413 were the process solution tanks and contained the Sealing Step II and Sealing Step III solutions. Because of the unavailability of process steam to this line, Tanks 409 and 413 were retrofitted with nine kilowatt over-the-side immersion heaters. Tank 409 required two heaters and Tank 413 required three heaters because of the higher solution operating temperature. Each process solution tank also had a continuous duty centrifugal pump mounted externally to provide recirculation and agitation. Tanks 410 and 414 were retrofitted with an air sparger to provide minimal agitation to the rinse water. The rinse tanks also contained small submersible pumps for transferring solution-specific rinse water as makeup water to the matching process solution tank. A leased DI water unit was located on site to provide DI water for the process solutions and the rinse waters.

Testing

The pilot line was operated at two sets of conditions: the initial MDA-E recommended conditions, and the improved, optimized conditions as stated earlier in the Optimization section. Each set of conditions was monitored daily and maintained as needed. The pH of both process solutions was monitored and maintained by the addition of nitric acid or potassium hydroxide. The pH of the Sealing Step II solution was monitored using a pH meter, while the Sealing Step III solution was monitored using commercial pH paper. A pH meter could not be used for the Step III solution because the silicate in solution would foul the probe. The strength of the Step II solution was determined by titration with a Ferrous Ammonium Sulfate solution. The endpoint was denoted by the disappearance of the purple color of the potassium permanganate solution to a clear, colorless solution. A fresh bath normally required 8.3 ± 0.2 ml, while a spent bath required only 5.4 ± 0.2 ml. Provided the titration indicated a spent bath, the solution was recharged by adding one gallon of concentrate to each 29 gallons of spent solution. The temperature of both process solutions was maintained using a commercially available PID logic controller with the maximum deviation set to ±5 F. Each process solution was mildly agitated to provide uniform mixing and a constant temperature profile.

The steel test panels were hung on a rack fabricated out of high temperature Teflon®, which was supported by a hoist normally used for dipping parts in the plating solutions. The panels were processed through the pilot line and allowed to air dry. The rack of eight panels was immersed in the Sealing Step II solution for three minutes followed by immersion in a separate DI water bath for one minute. The panels were then immersed in the Sealing Step III solution for one minute followed by immersion in DI water for one minute. The control panels coated with the current CCC were processed according to standard operating procedures used by the plating shop personnel. The panels were initially immersed in a hot water tank for approximately ten seconds to bring the panels to the CCC solution temperature, followed by immersion in the chromate conversion coating solution for five minutes. The panels were then immersed in a cold water rinse tank for approximately ten seconds and allowed to air dry. After allowing to air dry, all panels were individually wrapped in white, lint-free tissue and packaged for shipment.

Disposal

The specification sheet for each of the Sanchem chemicals indicates that upon neutralization, the resultant solutions may be dispensed to an Industrial Wastewater Treatment Plant (IWTP), or the sanitary sewer. The Sealing Step II solution's purple color was chemically reduced to colorless manganese (II) by acidifying the bath and adding Ferrous Sulfate until the purple color disappeared. The resultant solution was then sent to IWTP No.2. Because of stipulations at the plating shop and IWTP No.2, the Sealing Step III solution was drummed and discarded at IWTP No.1. The reason for separate disposal was that IWTP No.2 could not accept any organics and the Step III solution contains a trace amount (<10ppm) of an organic, which is used as a stabilizer and silicate precipitant coupling agent.

EMD TEST RESULTS

The results of the tests conducted using the pilot line at WR-ALC are described below. All Salt Fog testing has been completed, along with the Primer Adhesion, and Fuel Resistance. The Contact Electrical Resistance testing is currently being conducted and results are expected by October, 1998.

Neutral Salt Fog

Test panels were prepared by masking the backs, edges, mounting holes, and a one-eighth inch perimeter on the face. Panels were then exposed to a neutral salt fog following ASTM B117 and using an exposure angle of 15 degrees from vertical. In accordance with the requirements of MIL-C-83488, any appearance of red rust products from the base metal would indicate failure.

The ten EMD qualification test panels prepared using the initial recommended Sanchem process conditions and two panels processed with chromate conversion all passed the 672 hour mark without showing corrosion of the base AISI 4130 steel, thus meeting the requirement of a MIL-C-83488 Class 1, Type II coating.

The ten EMD qualification test panels prepared using the improved Sanchem process conditions and two panels processed with chromate conversion both passed the 672 hour mark without showing corrosion of the base AISI 4130 steel, thus meeting the requirement of MIL-C-83488 for a Class 1, Type II coating. All panels passed 1344 hours of neutral salt fog testing, or double the requirements of MIL-C-83488.

Primer Adhesion

All 48 panels coated with the epoxy primer passed both wet and dry adhesion testing based on a category. Of the 24 test panels coated with polyurethane primer, all passed the dry adhesion test, but 14 of the 20 panels that were processed through the Sanchem process failed the wet adhesion test. The four panels with a chromate conversion coating passed the wet adhesion test. There did not appear to be any correlation between the primer adhesion failures and the Sanchem process conditions used.

The importance of the polyurethane primer adhesion is unknown at this time. It is believed that the utilization of polyurethane primers on components with IVD aluminum would be limited, possibly applying only to fasteners used on aircraft exterior panels. However, once installed on the aircraft, the fastener heads would be treated along with rest of the skin during preparation for primer application.

Fuel Resistance

Fuel Resistance testing was completed on test panels that were conversion coated with both the chromate and non-chromate processes (i.e., non-painted set) and panels that were conversion coated and then painted with two different T.O. 1-1-8 approved primer-topcoat combinations. Respective panel sets were immersion tested in JP-8 +100 aviation fuel that was maintained at 75 F and 140 F for 14 days. The fuel resistance of the conversion coatings alone, and the complete coating system (i.e., conversion coating + primer + topcoat) was assessed using visual/microscopic inspections throughout the exposure period and scratch hardness.

Results obtained from this testing indicate that the fuel resistance of the non-chromate conversion coating is comparable to the resistance afforded by the MIL-C-5541 chromate coating. There was a slight staining or discoloration of areas on panels coated with the former process and tested with the 140 F fuel after 14 days of testing. No conversion coating or IVD aluminum coating damage was noted in these discolored areas.

All results obtained from the fuel exposure testing conducted on panels that were conversion coated, primed and then top-coated also confirm that the inherent fuel resistance of the two different conversion coatings is identical. Specifically, the testing of painted panels failed to identify major coating defects as a result of exposure to the fuel at two different temperatures. Data collected from the scratch hardness testing conducted on the two sets of coated panels before and after exposure to the heated and ambient fuel solutions also failed to identify differences in the fuel resistance of the conversion coatings.

SCRATCH REPAIR

The objective of this task was to verify that commercially available touch-up coatings could be used to repair the non-chromate conversion coating applied to IVD aluminum which was locally damaged or scratched in service. In addition, these candidate repair methods would offer comparable corrosion protection as the current chromate conversion coating. Test panels were prepared at WR-ALC and Sanchem with the MIL-C-5541 chromate conversion coating and Safegard™ non-chromate conversion coating processes, respectively. The test surfaces of all panels included both single line scribes and scratch repair areas that were treated with each of the candidate touch-up coatings. Application and curing procedures included both heated and ambient temperature air drying. Testing of the candidate touch-up coatings included a 14-day exposure to an ASTM B117 neutral salt fog environment. Visual inspections of the scribe and scratch repair areas on the panels were conducted at 7 and 14-day intervals. All candidate coatings were selected on the basis of corrosion resistance and ease of application or use. The three candidate coatings were Henkel TD1154L, C-Tech Guard-Through M, and ProCoat Brugal E-713.

Results obtained from this investigation indicate that the chromate containing Permatreat 684 coating provided adequate corrosion protection to IVD aluminum exposed within both the scribe and scratch repair areas of test panels. The recommended candidate for the non-chromate touch-up, based on ease of application and corrosion resistance performance, was the Henkel TD1154L coating. The performance of this coating was similar to the Permatreat 684 chromate control. The effect of drying for the Henkel coating does not appear to influence the performance of the coating, therefore, it is recommended that this coating be applied by brush to the damaged area and allowed to air dry prior to being returned to service.

COATING REMOVAL

This task was designed to verify that the current production coating removal processes can be utilized to strip IVD aluminum that has been conversion coated with the SafeGard™ process. Test panels were prepared with the chromate conversion coating or with the SafeGard™ process. Panels were then stripped using the two approved production removal processes: aluminum oxide grit blast and caustic strip. The caustic strip was performed using both fresh and seasoned baths. The surfaces of the stripped panels were then analyzed using scanning electron microscopy (SEM) and electron dispersion spectroscopy (EDS). The surface conditions of the chromated panels were compared to the surfaces of SafeGard™ panels to investigate differences.

The results of the coating removal testing indicate that there is <u>not</u> a significant difference between the two conversion coating with respect to the residual surface deposits after grit blasting, or with caustic stripping using either fresh or seasoned baths. The major difference is in the removal time required using the caustic stripper, based on the gassing period, which was significantly longer and more variable for SafeGard™ than for chromate. This result is consistent with the expected relative reactivity of the coatings to caustic. Therefore, additional processing time, or perhaps and increase in caustic concentration, bath temperature, or both may be required for SafeGard™ realtive to chromate to achieve the same production rate. It should be noted that significant differences in surface elemental composition for the two strip methods were observed. Caustic stripping removed the IVD aluminum completely, while grit blasting left an aluminum layer on the steel. Grit blasting also left grains of blasting media embedded in the surface of the steel. These observations were independent of the two coating systems.

FUTURE WORK

After completion of the EMD qualification tests, tasks to be completed include an Economic Cost/Benefit Analysis, Regulatory Research and Verification, and submission of the Final Report. It is extremely important from a needs/readiness standpoint that this project be completed and proceed to the next level, or System Prototype Demonstration/Validation. It would also be of tremendous benefit to the Air Force, and possibly other branches of the military, if this coating system were demonstrated and validated for aluminum alloys. This would allow a complete block change through a weapon system manufacturer to qualify this coating system as a replacement for the current chromate conversion coating.